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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Torsten Gottschalk-Gaudig et al.

Group Art Unit: 1796

Serial No.: 10/599,026

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For: PARTICLE-STABILISED EMULSIONS

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DECLARATION OF DR. TORSTEN GOTTSCHALK-GAUDIG

Mail Stop Amendment
Commissioner for Patents
U.S. Patent & Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Dr. Torsten Gottschalk-Gaudig, do hereby declare and state as follows:

1. I am a coinventor of the claimed subject matter of U.S. Application Serial No. 10/599,026, and am familiar with the contents of the application, the Office Action received from the United States Patent and Trademark Office, and the references cited by the Patent Examiner.

2. I studied organic chemistry and coordination chemistry from 1987 to 1994 at the Universität Erlangen-Nürnberg, and from 1994 to 1997 pursued my doctoral studies, under the supervision of Prof. D. Sellmann, Institut für Anorganische Chemie II, at the same university. I achieved my Ph.D *summa cum laude*, my thesis titled "Activation and Stabilization of Small Molecules by Ruthenium Complexes Bearing Tetradeятate Thioether-Thiolate Ligands. I pursued post doctoral studies under Prof. K.G. Caulton at Indiana University during 1998 to 1999, and then under Prof. Sellmann at the Universität Erlangen-

Nürnberg during 1999-2000. In November of 2000 I accepted the position of Research and Development Manager, SILICA, at Wacker Chemie AG, and since June of 2003 I have been Platform Manager, SILICA, for that company. I am the author or co-author of some 26 scientific publications, and am a named inventor for numerous patent families filed worldwide. A list of publications and patent families is attached.

3. Barthel U.S. Patent No. 5,686,054 is directed to highly hydrophobicized silica in which virtually all surface silanol groups are blocked, rendering this silica highly apolar. Such highly apolar silica is not water wettable, and merely floats on the surface of water when added thereto. Such apolar silica is incapable of use as a dispersant in preparing emulsions containing an aqueous phase and an oily phase. Silica which is at least partly water wettable is required in such applications.

4. Barthel U.S. Published Application No. 2003/0175317 A1 ("Barthel") discloses the use of partly water wettable silica for use in preparing multiple emulsions. When the process of *Barthel* is employed to produce emulsions, a problem of creaming of the emulsion occurs. The present invention is directed to preparation of emulsions with a low relative viscosity in which coalescence and creaming are both eliminated or sharply reduced, so that the emulsions will be commercially useful (and thus commercially acceptable) after shipping and/or storage. Previously, such stable emulsions could only be made through the use of organic emulsifiers. The emulsions can be used as such, or may be compounded with other ingredients to make numerous products, as reflected in the claims.

To show the difference between emulsions prepared by the process of *Barthel* and that of the subject invention, the following side-by-side examples were performed under my direction. Note that in both examples, the same partly hydrophobicized silica is used, and all ingredients are used in the same amounts. Yet, the emulsions have totally different properties. Additional examples using other partly hydrophobic silicas and different aqueous and oil phases would be expected to behave in similar fashion, as there is no technological reason to suspect otherwise. The keys to the emulsion stability are the use of the partly hydrophobic silica as the dispersant, and its addition to only a portion of the continuous phase

to form a viscous dispersion, following which the disperse phase is added, and lastly the remainder of the continuous phase is added.

Example 1 according to US 20030175317 (Barthel et al.) (non-inventive):

A stainless steel beaker is charged with 56 g of an aqueous dispersion containing pyrogenic silica HKS® D ($200 \text{ m}^2/\text{g}$ BET surface area; 71% residual silanol content) and 107 g of DI water resulting in a low viscosity dispersion. While stirring at 10000 rpm using an Ultraturrax® mixer, 150 g of polydimethylsiloxane (specific viscosity 100 mPas) was added slowly. After complete addition of polydimethylsiloxane the mixture was mixed for additional 5 minutes resulting in a white emulsion. Analytical data are summarized in Table 1.

Example 2 according to the invention:

A stainless steel beaker is charged with 56 g of an aqueous dispersion containing pyrogenic silica HKS® D ($200 \text{ m}^2/\text{g}$ BET surface area; 71% residual silanol content) and 21 g of DI water in order to obtain a water content of 30 wt% in the preemulsion resulting in a highly viscous dispersion. While stirring at 10000 rpm using an Ultraturrax® mixer, 150 g of polydimethylsiloxane (specific viscosity 100 mPas) was added slowly. After complete addition of polydimethylsiloxane the mixture was mixed for additional 5 minutes. Finally, 86 g of DI water was added while stirring, resulting in a white emulsion. Analytical data are summarized in Table 1.

Table 1:

	Example 1	Example 2
Type	O/W	O/W
Φ_w/Φ_o	50/50	50/50
$d_{05} / \mu\text{m}$	1.7	1.2
$d_{50} / \mu\text{m}$	6.9	5.0
$d_{95} / \mu\text{m}$	30.0	9.2
$V_{sep} / \%$	30	< 1

The emulsion obtained from example 1 reveals a much broader droplet size distribution with a d_{95} of 30 μm compared to ca. 9 μm for the emulsion from example 2. Due to this broad droplet size distribution emulsion 1 shows strong phase separation with a depleted volume fraction V_{sep} of 30%. The phase separation (creaming) can be explained by the strong buoyancy of the large oil droplets. However, emulsion 2 shows no segregation.

In order to visualize the difference between emulsion 1 and emulsion 2 and therefore the advantage of the inventive process for making particle stabilized emulsions Figure 1 shows the results of droplet size measurements on emulsion 1 (= OG-131-A; red trace) versus emulsion 2 (= OG-131-B; blue trace). Again, a much broader droplet size distribution for emulsion 1 is seen.

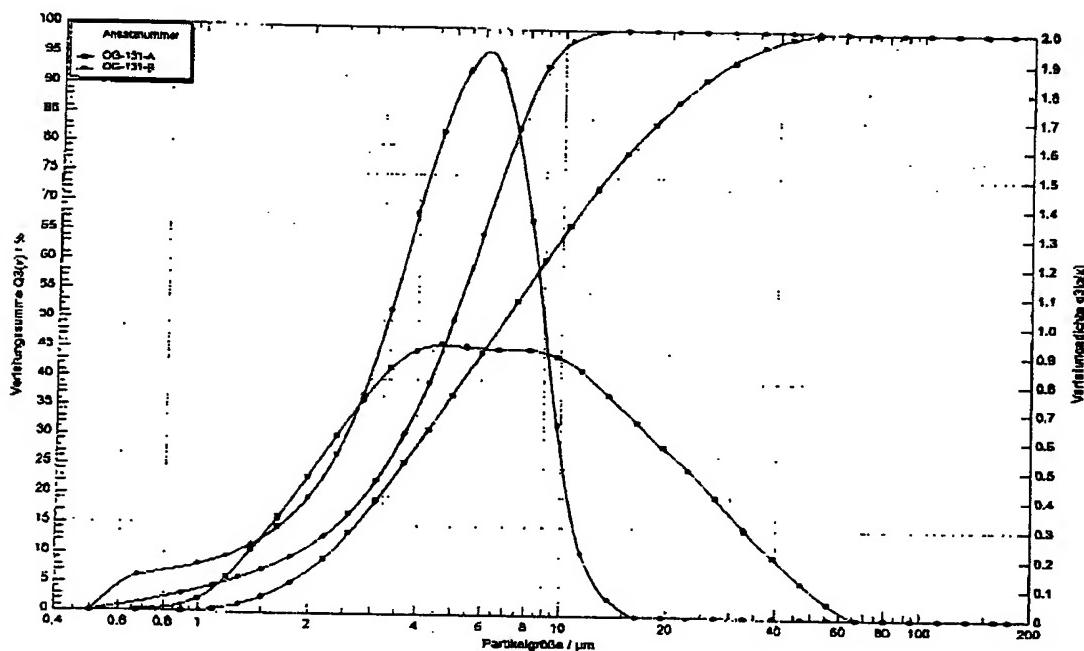


Figure 1: Droplet size distribution of emulsion 1 (= OG-131-A; red trace) emulsion 2 (= OG-131-B; blue trace) obtained by means of Fraunhofer laser light scattering.

This result is also supported by light microscopy (Figure 2) which clearly shows a broad droplet size distribution for emulsion 1 (Figure 2a) and a tight distribution for emulsion 2.

(Figure 2b).

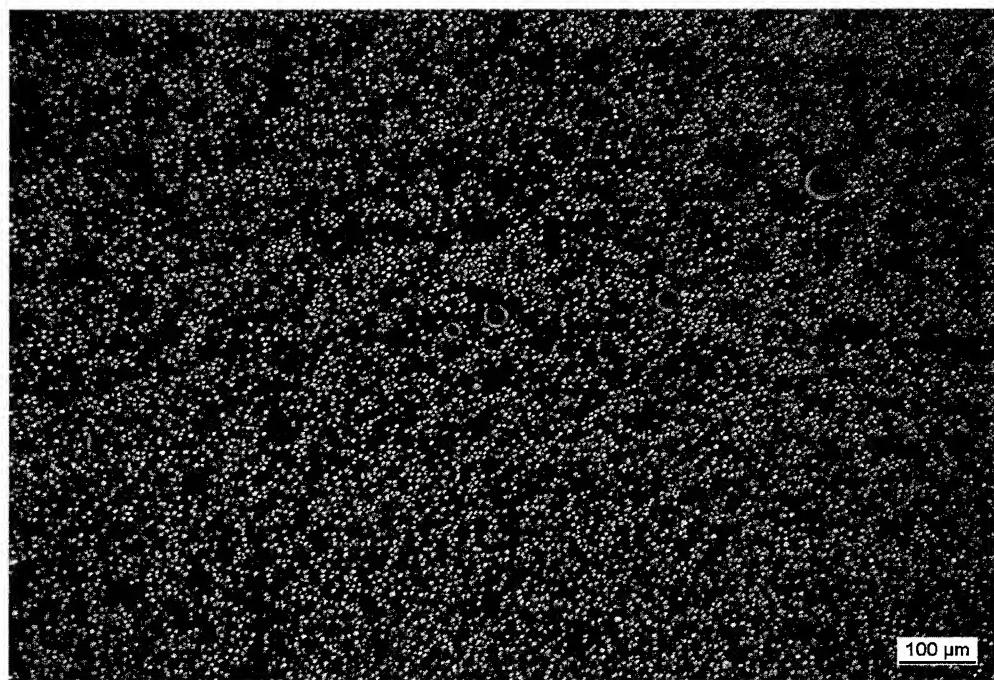
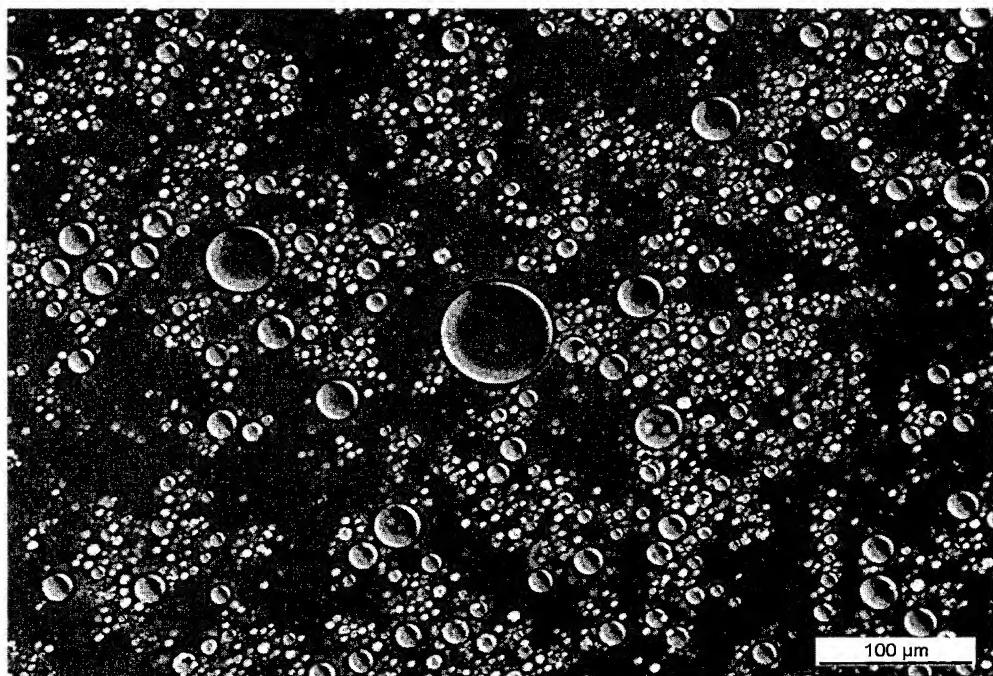


Figure 2: a) light microscopy of emulsion 1 and, b) light microscopy of emulsion 2.

The particle size distribution also strongly influences the intrinsic viscosity, which is the form factor used in the Krieger-Dougherty equation $\eta_{ref} = (1-\Phi/0.74)^{[(\eta)-0.74]}$ (see claim 10 of the present application). From theoretical calculations, an intrinsic viscosity $[\eta]$ of 2.5 is obtained for perfectly spherical and monodisperse particles. A broad particle size distribution results in an increase of $[\eta]$. Accordingly, the tight droplet size distribution of emulsion 2 results in an intrinsic viscosity of 5.7. For emulsion 1, which shows a broad droplet size distribution, an intrinsic viscosity of 23.4 is obtained.

The experiments clearly show the huge influence of the new process on emulsion properties. For commercial products, stability against phase separation is a must. This is only achieved by employing the inventive process according to the present patent application.

The above side-by-side comparisons confirm that the process of *Barthel* cannot be used to prepare emulsions which are simultaneously of low relative viscosity and also stable with respect to coalescence and creaming. That these characteristics could be obtained by use of the claimed process is totally surprising and unexpected, and is certainly not predictable. *Barthel* does not disclose, nor does he teach or suggest the claimed process, nor the claimed product.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.



Dr. Torsten Gottschalk-Gaudig et al.

Dated: 05.08.2010

List of publications:

Scientific Publications:

1. Ridaoui, H.; Donnet, J.-B.; Balard, H.; Kellou, H.; Hamdi, B.; Barthel, H.; Gottschalk-Gaudig, T.; Legrand, A.-P. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* (2008), 330(1), 80-85
2. Donnet, J.-B.; Balard, H.; Nedjarl, N.; Hamdi, B.; Barthel, H.; Gottschalk-Gaudig, T. *Journal of Colloid and Interface Science* (2008), 328(1), 15-19
3. Kaetzel, U.; Gottschalk-Gaudig, T.; Stintz, M.; Barthel, H. *Chemie Ingenieur Technik* (2008), 80(9), 1408
4. Kellou, H.; Hamdi, B.; Brendle, E.; Gottschalk-Gaudig, T.; Barthel, H.; Ridaoui, H.; Balard, H.; Donnet, J.-B. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* (2008), 327(1-3), 90-94
5. Donnet, J.-B.; Ridaoui, H.; Balard, H.; Barthel, H.; Gottschalk-Gaudig, T. *Journal of Colloid and Interface Science* (2008), 325(1), 101-106
6. Kaetzel, U.; Vorbau, M.; Stintz, M.; Gottschalk-Gaudig, T.; Barthel, H. *Particle & Particle Systems Characterization* (2008), 25(1), 19-30
7. Kaetzel, U.; Bedrich, R.; Stintz, M.; Ketzmerick, R.; Gottschalk-Gaudig, T.; Barthel, H. *Particle & Particle Systems Characterization* (2008), 25(1), 9-18
8. Gottschalk-Gaudig, T.; Barthel, H. *Organosilicon Chemistry VI: From Molecules to Materials* (2005), Volume 2, 902-909.
9. Zhuang, Y.; Sampurno, Y. A.; Sudargho, F.; Steward, G.; Barthel, H.; Mayer, E.-P.; Gottschalk-Gaudig, T.; Stintz, M.; Kaetzel, U.; Nogowski, A.; Goldstein, M.; Phillipsson, A. *Materials Research Society Symposium Proceedings* (2007), 991(Advances Challenges in Chemical Mechanical Planarization), 233-238
10. Horozov, T. S.; Binks, B. P.; Gottschalk-Gaudig, T. *Physical Chemistry Chemical Physics* (2007), 9(48), 6398-6404
11. Katzel, U.; Richter, T.; Stintz, M.; Barthel, H.; Gottschalk-Gaudig, T. *Physical Review E: Statistical, Nonlinear, and Soft Matter Physics* (2007), 76(3-1)
12. Dreyer, M.; Gottschalk-Gaudig, T.; Barthel, H. *European Coatings Journal* (2007), (7-8), 39-44
13. Barthel, H.; Gottschalk-Gaudig, T.; Dreyer, M. *Surfactant Science Series* (2007), 137(Powders and Fibers), 565-609
14. Dreyer, M.; Gottschalk-Gaudig, T.; Barthel, H. *Farbe + Lack* (2007), 113(4), 28-129
15. Kaetzel, U.; Stintz, M.; Babick, F.; Barthel, H.; Gottschalk-Gaudig, T. *AIChE Spring National Meeting, Conference Proceedings*, Orlando, FL, United States, Apr. 23-27, 2006 (2006)
16. Barthel, H.; Dreyer, M.; Gottschalk-Gaudig, T.; Litvinov, V.; Nikitina, E. *Organosilicon Chemis-*

- try V: From Molecules to Materials (2003), 752-766.
- 17. Barthel, H.; Dreyer, M.; Gottschalk-Gaudig, T.; Litvinov, V.; Nikitina, E. Macromolecular Symposia (2002), 187, 573-584
 - 18. Sellmann, D.; Gottschalk-Gaudig, T.; Häussinger, D.; Heinemann, F. W.; Hess, B. A. Chemistry-A European Journal (2001), 7(10), 2099-2103
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 - 25. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. Inorganica Chimica Acta (1998), 269(1), 63-72
 - 26. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W.; Knoch F. Chemische Berichte/Recueil (1997), 130(5), 571-579

Patents:

- 1. EP1433749 Process for the production of wettable, gentle hydrophobic and finely dispersed silica comprising a silylated surface
- 2. EP1473296 Silica treated with alpha-silanes and process for its manufacturing
- 3. DE10349082 Water based dispersions and/or emulsions of RTV-1 silicone sealants stabilized by (partial) silylated pyrogenic silica which do not cleave off VOC or contain tensides
- 4. DE10360464 Dispersions of silica comprising at least two different types of silica particles having different isoelectrical points
- 5. WO05092989 Emulsions of W/O- / O/W-typ comprising an oil phase, a water phase and sintered aggregates of pyrogenic silica at their interphase

6. WO06018144 Particles comprising a core consisting of metal oxides, metal/silicon oxides, silicon dioxide and/or silicone resins having protected isocyanate groups on the surface
7. WO06018112 pyrogenic silica stabilized emulsion comprising low amounts of electrolytes showing enhanced flowing properties
8. WO06081979 Hydroxy alkyl functional particles as filler obtainable by conversion of metal oxide, organo polysiloxane resins and/or colloidal particles with cyclic organo siloxanes in the presence of water or alcohol
9. WO06058657 Cationic silica for dispersions for the synthesis of coatings for ink jet media
10. WO06097240 Dispersions of partially hydrophobized silica for water based resins and adhesives
11. WO07012547 Sterical stabilized silica dispersed in organic or aqueous matrix comprising high filler amounts for the use in scratch resistant coatings and nano-composite adhesives
12. WO06084629 Composition for coatings comprising particles having protected isocyanato groups at the surface
13. WO08000302 Process for the production of pyrogenic silica using a combustion chamber comprising a cooling to produce silica with low amounts of impurity atoms and low amounts coarse-grained particles
14. WO07048691 Zwitterionic particles modified with ammonium-alkyl-sulfonated siloxanes and their use as filler in composite materials for the production of membranes
15. EP1845136 Alkylsilane-modified pyrogenic silica as rheological additive basic media like amine hardeners for epoxy
16. WO07113095 Core-shell particles with a substructure inducing selfcleaning properties